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U.S. DEPARTMENT OF COMMERCE
PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

UC18024

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (if known, see 37 C.F.R. 1.5)

10/031803

INTERNATIONAL APPLICATION NO.
PCT/US00/15754

INTERNATIONAL FILING DATE
08 June 2000

PRIORITY DATE CLAIMED
08 June 1999

TITLE OF INVENTION

WATERBORNE THICKENERS AND DISPERSANTS HAVING IMPROVED CHEMICAL RESISTANCE

APPLICANT(S) FOR DO/EO/US

Keith R. Olesen; Gerald A. Vandezande

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☒ is not required, as the application was filed in the United States receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the Annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 15. below concern other document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ A FIRST preliminary amendment.
- ☐ A SECOND or SUBSEQUENT preliminary amendment.
13. ☐ A substitute specification.
14. ☐ A change of power of attorney and/or address letter.
15. ☐ Other items or information:

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.50) <div style="text-align: center; font-size: 1.2em; font-weight: bold;">10/031803</div>		INTERNATIONAL APPLICATION NO PCT/US00/15754		ATTORNEY'S DOCKET NUMBER UC18024	
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17. <input checked="" type="checkbox"/> The following fees are submitted: <div style="margin-left: 20px;"> Basic National Fee (37 CFR 1.492(a)(1)-(5)): Search Report has been prepared by the EPO or JPO \$ 890.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) \$ 710.00 No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$ 740.00 Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445 (a)(2)) paid to USPTO \$ 1,040.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$ 100.00 </div> <div style="text-align: right; margin-top: 10px;"> ENTER APPROPRIATE BASIC FEE AMOUNT = </div>				CALCULATIONS		PTO USE ONLY	
				\$ 890.00			
Surcharge of \$ 130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$ 130.00			
Claims	Number Filed	Number Extra	Rate				
Total Claim	16 - 20 =	0	X \$ 18.00	\$ 0.00			
Independent Claims	2 - 3 =	0	X \$ 84.00	\$ 0.00			
Multiple dependent claim(s) (if applicable)				\$ 0.00			
Processing fee of \$ 0 for furnishing the English Translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$ 0.00			
TOTAL NATIONAL FEE =				\$ 1,020.00			
				Amount to be refunded: \$			
				charged: \$			

a. <input type="checkbox"/> A check in the amount of \$ _____ to cover the above fees is enclosed. b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. 04-1512 in the amount of \$ 1,020.00 to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 04-1512 . A duplicate copy of this sheet is enclosed.	
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Note: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO: Graham E. Taylor The Dow Chemical Company Intellectual Property P.O. Box 1967 Midland, Michigan 48641-1967 UNITED STATES OF AMERICA Phone: 989-636-5655	Signature: <div style="text-align: center;">Edward W. Black</div> <div style="text-align: right;">, Registration No. 36,454</div> Date: <u>06 November 2001</u>
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November 6, 2001

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**THIS APPLICATION IS THE ENTRY INTO THE
NATIONAL PHASE UNDER 35 U.S.C. 371**

Applicant(s): Keith R. Olesen; Gerald A. Vandezande

International Application No. PCT/US00/15754

International Filing Date: 08 June 2000

Priority Date Claimed: 08 June 1999

Title: WATERBORNE THICKENERS AND DISPERSANTS HAVING IMPROVED CHEMICAL
RESISTANCE

Attorney's Docket No.: UC18024

WATERBORNE THICKENERS AND DISPERSANTS
HAVING IMPROVED CHEMICAL RESISTANCE

FIELD OF THE INVENTION

The present invention relates to latex polymers having crosslinking functionality which are suitable for use, for example, as thickeners and dispersants in latex coating compositions.

BACKGROUND OF THE INVENTION

Latex paint coatings are typically applied to substrates and dried to form continuous films for decorative purposes as well as to protect the substrate. Such paint coatings are often applied to architectural interior or exterior surfaces, where the coatings are sufficiently fluid to flow out, form a continuous paint film, and dry at ambient temperatures.

A latex paint ordinarily comprises an organic polymeric binder, i.e., latex polymer, pigments, and various paint additives. In dried paint films, the polymeric binder functions as a binder for the pigments and provides adhesion of the dried paint film to the substrate. The pigments may be organic or inorganic and functionally contribute to opacity and color in addition to durability and hardness, although some paints contain little or no opacifying pigments and are described as clear coatings. The manufacture of paints involves the preparation of a polymeric binder, mixing of component materials, grinding of pigments in a dispersant medium, and thinning to commercial standards.

Conventional latex paints are widely used because they provide low volatile organic compound emission and because they allow easier clean up than solvent borne coatings. However, when compared to solvent borne coating systems, typical latex coatings lack the chemical resistance provided by such solvent borne coatings.

Crosslinking of polymer coatings typically enhances the coating's chemical resistance as well as the cohesive strength, abrasion resistance, and exterior durability. A common way to crosslink a polymer is to react a functional group containing reactive polymer with an external multifunctional crosslinker. The external crosslinker can be pre-mixed with the reactive polymer (commonly called a one-package system) or, alternatively, it can be mixed with the reactive polymer immediately prior to the application (commonly called a two-package system). One-package systems are often desired because of their simplicity and ease of handling.

Crosslinking functionality has been incorporated into latexes to allow for crosslinking in both one stage polymer and two stage polymer systems. For example, U.S. Patent No. 5,326,843 describes a latex in which hydroxyethyl acrylate is added to the set of polymerizable monomers to impart reactive functionality on a one stage polymer system. The hydroxyl functionality can react with aminoplasts and polyisocyanates to form a cured film. Crosslinkable latexes are also disclosed, for example, in WO 95/29963 and WO 95/29944 (two stage latexes), and U.S. Patent Nos. 4,144,212, 4,522,962 and 5,414,041 (single stage latexes).

In addition to imparting crosslinking functionality to binder polymers, further improvements in latex coating compositions are desired which can provide enhanced properties, e.g., chemical resistance.

SUMMARY OF THE INVENTION

This invention is directed to thickeners and dispersants for waterborne coatings which can provide improved properties, e.g., chemical resistance. It has now been found that latex coating compositions having superior properties, e.g., chemical resistance, can

be produced by utilizing in the coating compositions certain thickeners or dispersants, or both, having crosslinking functionality or increased levels of macromonomers. Optionally, a latex binder having crosslinking groups can also be used. The crosslinking, or increased macromonomer levels, groups present in the thickener or dispersant can be adjusted to optimize the desired performance properties of the coating composition. More specifically, the latex coating compositions can be tailor made to have increased chemical resistance, corrosion resistance, humidity resistance and/or adhesion to a particular substrate by altering the levels of crosslinking, or macromonomer, on the thickener or dispersant. The latex coating compositions of the present invention may, for example, be ambient cured, oven cured or radiation cured.

The present invention provides polymers which can be useful in compositions such as architectural coatings, industrial and automotive coatings, sealants, adhesives, paper coating compositions, inks, varnishes and the like.

DETAILED DESCRIPTION OF THE INVENTION

The latex polymers suitable for use as binders in accordance with the present invention include those polymers polymerized from one or more suitable monomers. Typically, the binders are polymerized from one or more copolymerizable monoethylenically unsaturated monomers such as, for example, vinyl monomers and acrylic monomers.

The vinyl monomers suitable for use in accordance with the present invention include any compounds having vinyl functionality, i.e., ethylenic unsaturation, exclusive of compounds having acrylic functionality, e.g., acrylic acid, methacrylic acid, esters of such acids, acrylonitrile and acrylamides. Preferably, the vinyl monomers are selected from the group consisting of vinyl esters, vinyl aromatic

hydrocarbons, vinyl aliphatic hydrocarbons, vinyl alkyl ethers and mixtures thereof.

Suitable vinyl monomers include vinyl esters, such as, for example, vinyl propionate, vinyl laurate, vinyl pivalate, vinyl nonanoate, vinyl decanoate, vinyl neodecanoate, vinyl butyrates, vinyl benzoates, vinyl isopropyl acetates and similar vinyl esters; vinyl aromatic hydrocarbons, such as, for example, styrene, methyl styrenes and similar lower alkyl styrenes, chlorostyrene, vinyl toluene, vinyl naphthalene and divinyl benzene; vinyl aliphatic hydrocarbon monomers, such as, for example, vinyl chloride and vinylidene chloride as well as alpha olefins such as, for example, ethylene, propylene, isobutylene, as well as conjugated dienes such as 1,3 butadiene, methyl-2-butadiene, 1,3-piperylene, 2,3-dimethyl butadiene, isoprene, cyclohexene, cyclopentadiene, and dicyclopentadiene; and vinyl alkyl ethers, such as, for example, methyl vinyl ether, isopropyl vinyl ether, n-butyl vinyl ether, and isobutyl vinyl ether.

The acrylic monomers suitable for use in accordance with the present invention comprise any compounds having acrylic functionality. Preferred acrylic monomers are selected from the group consisting of alkyl acrylates, alkyl methacrylates, acrylate acids and methacrylate acids as well as aromatic derivatives of acrylic and methacrylic acid, acrylamides and acrylonitrile. Typically, the alkyl acrylate and methacrylic monomers (also referred to herein as "alkyl esters of acrylic or methacrylic acid") will have an alkyl ester portion containing from 1 to about 12, preferably about 1 to 5, carbon atoms per molecule.

Suitable acrylic monomers include, for example, methyl acrylate and methacrylate, ethyl acrylate and methacrylate, butylacrylate and methacrylate, propyl acrylate and methacrylate, 2-ethyl hexyl acrylate and methacrylate, cyclohexylacrylate and methacrylate, decyl acrylate

and methacrylate, isodecyl acrylate and methacrylate, benzyl acrylate and methacrylate, isobornyl acrylate and methacrylate, neopentyl acrylate and methacrylate, 1-adamatyl methacrylate and various reaction products such as butyl, phenyl, and cresyl glycidyl ethers reacted with acrylic and methacrylic acids, hydroxyl alkyl acrylates and methacrylates such as hydroxyethyl and hydroxypropyl acrylates and methacrylates, amino acrylates, methacrylates. Suitable acid or anhydride functional monomers include acrylic acid, methacrylic acid, ethacrylic acid, alpha-chloroacrylic acid, crotonic acid, citraconic acid, mesaconic acid, itaconic acid, maleic acid, fumaric acid, 3-acrylamido-3-methylbutanoic, acrylic anhydride, methacrylic anhydride, ethacrylic anhydride, crotonic anhydride, citraconic anhydride, mesaconic anhydride, itaconic anhydride, maleic anhydride, fumaric anhydride, p-styrene carboxylic acid, p-styrene sulfonic acids, vinyl sulfonic acid, 2-sulfoethyl methacrylate, 3-sulfopropyl methacrylate, 3-sulfopropylacrylate, 2-acrylamido-2-methylpropane sulfonic acid, and the like including mixtures thereof.

In addition to the specific monomers described above, those skilled in the art will recognize that other monomers such as, for example, allylic monomers, or monomers which impart wet adhesion, e.g., methacrylamidoethyl ethylene urea, can be used in place of, or in addition to, the specifically described monomers in the preparation of the binders (as well as the dispersants and thickeners hereinafter described). Further details concerning such other monomers suitable for copolymerization in accordance with the present invention are known to those skilled in the art. The amount of such other monomers is dependent on the particular monomers and their intended function, which amount can be determined by those skilled in the art.

Optionally, the binder polymers of the present invention may have crosslinking functionality. In this aspect of the invention, at least one of the monomers used to polymerize the binder is an ethylenically unsaturated monomer containing "latent crosslinking" or "post crosslinking" capabilities, which as used herein means a monomer which possesses the ability to further react, e.g., with a crosslinking agent, some time after initial formation of the polymer. Activation of the crosslinking can occur through the application of energy, e.g., through heat or radiation. Also, drying can activate the crosslinking of the polymer through changes in pH, oxygen content or other changes that cause a reaction to occur. The particular method of achieving crosslinking in the binder polymer is not critical to the present invention. A variety of chemistries are known in the art to produce crosslinking in latexes.

Examples of monomers which effect crosslinking during film formation include carbonyl-containing monomers such as acrolein, methacrolein, diacetone acrylamide, diacetone methacrylamide and vinylaceto acetate. These monomers result in post crosslinking, for example, when the aqueous polymer emulsion also contains an appropriate added amount of a crosslinking agent. The crosslinking agent may be any compound, including polymers, whether or not soluble in the aqueous phase of the latex composition, which promotes the crosslinking of the binder polymer. The particular crosslinking agent is not critical to the present invention. Particularly suitable compounds of this type are the dihydrazides and trihydrazides of aliphatic and aromatic dicarboxylic acids of 2 to 20 carbon atoms. Examples of these are oxalic dihydrazide, adipic dihydrazide and sebacic dihydrazide.

Another monomer which produces post crosslinking is, for example, 2-acetoacetoxyethyl methacrylate (alone or in combination with other compounds, such as, for example, glyoxal).

Other monomers which are suitable for post crosslinking are those which contain hydrolyzable organosilicon bonds. Examples are methacryloyloxy-propyltrimethoxysilane and vinyltrimethoxysilane. Further suitable monomers are described, for example, in DE-A4341260. If the disperse polymer particles have carboxyl groups, post crosslinking can also be effected by adding metal salts having polyvalent cations (for example Mg, Ca, Zn or Zr salts).

Epoxy-, hydroxyl- and/or N-alkylol-containing monomers, for example, glycidyl acrylate, N-methylolacrylamide and -methacrylamide and monoesters of dihydric alcohols with α,β -monoethylenically unsaturated carboxylic acids of about 3 to 6 carbon atoms, such as hydroxyethyl, hydroxy-n-propyl or hydroxy-n-butyl acrylate and methacrylate are also suitable for post crosslinking.

The binder polymer of the present invention typically contains from about 0.5 to 10% by weight, based on the total weight of the polymer, of at least one monomer having crosslinking functionality, and preferably from about 1 to 6% by weight, based on the total weight of the polymer, of at least one monomer having crosslinking functionality. Preferably, the binder polymer comprises less than about 25 wt %, more preferably less than about 20 wt. % and most preferably less than about 15 wt. % of monomers having crosslinking functionality, said percentages based on the total weight of the binder polymer (i.e., total weight of monomers used to polymerize the first stage polymer and the second stage polymer).

Typically, the particle size of the binder polymers is from about 0.1 to 1.0 microns, preferably from about 0.2 to 0.4 microns and more

preferably from about 0.25 to 0.3 microns. The Tg of the binders of the present invention is typically from about -60 to 100°C preferably from about -30 to 70 °C and more preferably from about -15 to 60°C. As used herein, the term Tg" means polymer glass transition temperature.

Techniques for measuring the glass transition temperature of polymers are known to those skilled in the art. One such technique is, for example, differential scanning calorimetry. A particularly useful means of estimating the glass transition temperature of a polymer is that given by Fox,

$$1/T_{g(\text{polymer})} = x_1/T_{g_1} + x_2/T_{g_2} + x_3/T_{g_3} + \dots + x_n/T_{g_n} \quad (1)$$

where x_i is the weight fraction of component i in the copolymer and Tg_i is the homopolymer glass transition of component i. The homopolymer glass transition temperatures can be found in any publicly available source such as the Polymer Handbook. For example, the homopolymer glass transition temperatures for typical monomers are: vinyl acetate = -32°C, butyl acrylate = -54°C, and vinyl neodecanoate = -3°C and 2-ethylhexyl acrylate = -65°C.

Typically, the viscosity of the binders of the present invention is from about 20 to 3000 and preferably from about 50 to 1500 centipoise ("cP") measured with a 40 to 60 weight percent solids composition using a Brookfield Viscometer with a number 2 spindle at 60 revolutions per minute. The molecular weight of the binders of the present invention is typically from about 5×10^4 to 10^7 , preferably from about 200,000 to 1,000,000 grams per gram mole. Unless otherwise indicated, as used herein, the term "molecular weight" means number average molecular weight ("Mn"). Techniques for altering molecular weight are well known and include, for example, utilizing multifunctional monomers and chain

transfer agents. Techniques for measuring the number average molecular weight of latex polymers is known to those skilled in the art. One such technique is, for example, gel permeation chromatography. In the case of two stage polymers, unless otherwise indicated, the molecular weight refers to the molecular weight of the first stage polymer and the second stage polymer polymerized separately.

The binder polymers of the present invention may contain hydrophobic groups. The ethylenically unsaturated monomers described above can, for example, be polymerized with one or more macromonomers which are polymerizable in order to introduce hydrophobic groups. Such macromonomers comprise a hydrophobic portion and an alkoxyated portion which is polymerizable with the other monomers. U.S. Patent No. 4,703,080, the disclosure of which is incorporated herein by reference, describes hydrophobic binder resins. Preferred macromonomers are urethane monomers which comprise the reaction product of a monohydric surfactant and a monoethylenically unsaturated isocyanate. Such macromonomers are known to those skilled in the art.

In one aspect of the present invention, the binder polymer comprises an acid functional latex. Specific acid functional monomers suitable for use in accordance with the present invention include, for example, acrylic acid, methacrylic acid, and maleic acid.

A preferred vinyl acrylate binder resin comprises 40-60% by weight of a fatty acid vinyl ester, about 30-50% by weight of methylmethacrylate, about 0.5 to 10% by weight of diacetone acrylamide and about 0.5-5% by weight methacrylic acid, based on the total weight of the polymer.

A preferred acrylic binder resin comprises about 20-35% by weight butyl acrylate, 40-65% by weight methyl methacrylate, about 0.5-10% by

weight diacetone acrylamide, about 0.5-5% by weight methacrylic acid and about 5-10% by weight acrylonitrile, based on the total weight of the polymer.

In a preferred aspect of the invention, the binder is a two stage polymer comprising a first stage polymer and a second stage polymer.

The first stage polymer is made by an emulsion polymerization of a mixture of monomers comprising at least one carboxylic acid or anhydride functional monomer or monomer that imparts alkaline sensitivity to the first stage polymer, reacted with a variety of comonomers, optionally in the presence of a monomer having crosslinking functionality.

The amount of acid or anhydride functionality present in the first stage emulsion polymerization determines the degree of solubility of the first stage on addition of a base. A minimum amount of acid or anhydride functionality is needed to solubilize the polymer depending on the hydrophobicity of the comonomers, molecular weight of the polymer, chemical nature of the acid or anhydride monomer and sequence distribution of monomers in the polymers. The preferred weight of acid or anhydride functional monomers present in the first stage polymerization is at least about 2 weight percent, preferably at least 3 weight percent, more preferably about 5 weight percent to 50 percent; even more preferably from about 8 percent to 30 weight percent, and most preferably from about 10 percent to 20 weight percent, based on the total weight of monomers charged in the first stage reaction.

Illustrative of comonomers useful in the first stage polymerization are monomers such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, styrene, substituted styrene such as alpha methyl styrene, acrylonitrile, vinyl acetate, and other C₁-C₁₂ alkyl or hydroxy alkyl acrylates and methacrylates, vinyl 2-ethylhexanoate, vinyl propionate, vinyl neodecanoate, vinyl neononanoate, vinyl versatate, vinyl pivalate and the like, and/or mixtures thereof.

The first-stage polymer may have a variety of molecular weights. The molecular weight may be controlled by the addition of a suitable chain transfer agent as is known in the art. Examples of suitable chain transfer agents include, for example, alkyl mercaptans such as octyl mercaptan and decyl mercaptan, esters of mercaptoacetic acid, such as an ethyl ester of mercaptoacetic acid and 2-ethylhexyl ester of mercaptoacetic acid, and esters of mercapto- propionic acid, such as isooctyl ester of mercaptopropionic acid. In a preferred embodiment, the chain transfer agent may be selected from the group consisting of 2-ethylhexyl mercaptopropionate and iso-octyl mercaptopropionate or mixtures thereof. The Mn obtained in the first stage polymer typically ranges from 50,000 to 1,000,000 g/gmol. Preferably, the Mn of the first stage polymer is at least 50,000, more preferably from about 50,000 to 100,000 g/gmol.

In a preferred aspect of the invention, at the end of the first-stage polymerization, a neutralizing agent or base is added to the first

stage alkali-soluble polymer so as to swell, partially dissolve, or substantially dissolve the polymer. Suitable bases include ammonia, triethylamine, monoethanolamine, dimethylaminoethanol, ammonium hydroxide, sodium hydroxide, potassium hydroxide, calcium hydroxide and all other Group I A and II A hydroxides and the like. Propylene imine may also be effective for neutralization of the first-stage alkali-soluble polymer, while at the same time providing wet adhesion properties to the final product.

Based on equivalents of acid in the alkali-soluble polymer, 0.01 to 1.5 equivalents of base are typically added to the alkali-soluble polymer to swell, partially dissolve, or substantially dissolve the alkali-soluble polymer so as to form a stabilized dispersant medium for the second-stage polymerization.

In one aspect of the invention, the first stage latex polymer, as prepared, may be stored for later neutralization. In another aspect of the invention, the first stage polymer can be neutralized and used as a dispersant medium for other latex polymers including the second stage emulsion polymerization process of the present invention.

By using the first-stage polymer as the medium for a second stage emulsion polymerization of alkali-insoluble monomers, the final product has been found to exhibit improved film forming properties, chemical resistance properties and other characteristics.

Monomers useful for polymerization in the second-stage are preferably alkali-insoluble monomers, i.e., those which are substantially free of carboxylic acid or anhydride functionality, such as, for example, those which have acrylic, styrenic, vinyl or versatic

functionality. As used herein, the term "substantially free" means less than about 10 weight percent, preferably less than about 5 weight percent and more preferably less than about 2 weight percent, based on the total weight of the polymer.

Optional ingredients which may be included in the second stage polymerization of the alkali-insoluble polymers include, for example, other monomers such as vinyl esters, acid and/or anhydride functional monomers, crosslinkers, chain transfer agents, and others as known in the art. The Mn can range from 500 to 500,000 or greater to infinity if the appropriate chain transfer or crosslinking agents are employed. The crosslinking functionality is also optionally incorporated in the second stage polymerization to provide crosslinking properties to the final latex product; provided, however, that it is incorporated into at least one of the first stage polymer or the second stage polymer.

The desired ratio for polymerization of the second-stage monomer feed into the first stage polymer medium covers a wide range depending on the desired properties of the final latex composition, and the acid level in each stage. For example, the amount of first stage polymer incorporated into the second stage polymerization may be small when using a more highly carboxylated material [e.g., 10 parts per hundred resin, i.e., first stage plus second stage ("p.h.r.") of the first stage resin which contains 20% methacrylic acid] or larger amount when using a less carboxylated material [e.g., 20 p.h.r. of the first stage resin which contains 10% methacrylic acid]. Suitable ranges include from about 1:99 to about 99:1. Preferably the weight

ratio of second-stage monomer feed is from about 5:95 to 95:5, and most preferably from about 10:80 to 80:10.

The binders of the present invention may be used, for example, in architectural coatings, industrial and automotive coatings, sealants, adhesives, paper coating compositions, inks, varnishes and the like.

In paint formulations, the alkali-insoluble polymers dispersed in the first-stage neutralized polymer may be used at levels based on the weight of solids, ranging from about 5 percent to about 90 percent of the total weight of the paint formulation. Paint formulations prepared with these unique polymers have been found to exhibit excellent chemical resistant, high gloss and improved block resistance. The paint formulations may, in addition to the binders of this invention, contain conventional additives such as pigments, fillers, dispersants, wetting agents, coalescents, rheology modifiers (also referred to as "thickeners"), drying retarders, biocides, anti-foaming agents and the like. Details concerning the selection and amounts of specific ingredients used in paint formulations are known to those skilled in the art.

In accordance with the present invention, dispersants having crosslinking functionality, thickeners having crosslinking functionality, or both are provided.

Any suitable dispersants may be utilized in accordance with the present invention. Preferred dispersant polymers having crosslinking functionality suitable for use in accordance with the present invention comprise the reaction product of an unsaturated carboxylic acid monomer, a monoethylenically unsaturated monomer different from the carboxylic acid monomer, a macromonomer comprising a hydrophobic

portion and an alkoxyolated portion which is polymerizable with the other monomers, and a monomer having latent crosslinking functionality.

The unsaturated carboxylic acid monomers suitable for use in preparing the dispersants are typically α,β -monethylenically unsaturated carboxylic acids. Preferred carboxylic acid monomers are selected from the group consisting of acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, and mixtures thereof. Methacrylic acid is especially preferred. The concentration of the carboxylic acid monomer is typically from about 20 to 70 weight percent, preferably from about 20 to 50 weight percent and more preferably from about 35 to 45 weight percent based on the total weight of the polymer. The amount of the carboxylic acid monomer is preferably sufficient to provide a polymeric structure which will solubilize and provide viscosity enhancement when reacted with an alkali such as for example, sodium hydroxide.

In accordance with the present invention, the monoethylenically unsaturated monomer different from the carboxylic acid monomer preferably comprises an ethyl group. More preferably, this monomer is an acrylate. Most preferably, this monomer is ethyl acrylate. Typically, the amount of the monoethylenically unsaturated monomer different from carboxylic acid is from about 5 to 70 weight percent, preferably from about 10 to 50 weight percent based on the total weight of the polymer. Optionally, the dispersant may or may not contain a macromonomer. In the case where no macromonomer is employed, it may be replaced on an equal weight basis with ethyl acrylate, for example.

The macromonomers suitable for manufacturing the dispersant in accordance with the present invention comprise a hydrophobic portion

and an alkoxyated portion which is polymerizable with other monomer(s). As used herein, the term "macromonomer" means a polymerizable monomer which comprises the reaction product of two or more compounds. Such macromonomers include, for example, any alkoxyated, e.g., ethoxyated or propoxyated, monomers having ethylenic unsaturation and which are terminated by a hydrophobic fatty chain. Examples of unsaturated, polymerizable moieties include those selected from the group consisting of vinyl group containing moieties, methacryloyl, maleoyl, itaconoyl, crotonyl, an unsaturated urethane moiety, hemiester maleoyl, hemiester itaconoyl, $\text{CH}_2=\text{CHCH}_2\text{-O-}$, methacrylamido and substituted methacrylamido. Examples of hydrophobic moieties include those selected from the group consisting of alkyl, alkaryl, i.e., alkylaryl or aralkyl, or aryl, linear or branched, saturated or unsaturated, and having at least 1 carbon atom, preferably from about 1 to 30 carbon atoms per molecule.

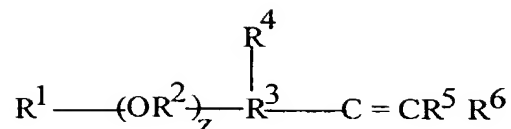
Preferred macromonomers are urethane monomers which comprise the reaction product of a monohydric surfactant and a monoethylenically unsaturated isocyanate. Preferably, the urethane monomer is a nonionic, urethane monomer which is the urethane reaction product of a monohydric, nonionic surfactant with a monoethylenically unsaturated monoisocyanate, preferably one lacking ester groups, e.g., alpha, alpha-dimethyl-m-isopropenyl benzyl isocyanate. The monohydric nonionic surfactants are themselves well known and are usually alkoxyated, e.g., ethoxyated, hydrophobes containing adducted ethylene oxide to provide the hydrophilic portion of the molecule. The hydrophobes are usually aliphatic alcohols or alkyl phenols in which a carbon chain containing at least 1 carbon atom, preferably about 1 to 30 carbon atoms, provides the hydrophobic portion of the surfactant. These surfactants are illustrated by ethylene oxide

adducts of dodecyl alcohol or octyl or nonyl phenol which are available in commerce and which contain about 5 to about 150, preferably 25 to 60 moles of ethylene oxide per mole of hydrophobe. Other hydrophobic substituents, such as complex hydrophobes, disclosed for example in U.S. Patent 5,488,180 issued January 30, 1996, are suitable for use in accordance with the present invention.

The monoethylenically unsaturated isocyanates suitable for use in preparing the urethane monomers can be any isocyanates effective to form the desired urethane linkage. Preferably, the isocyanate is a monoethylenically unsaturated monoisocyanate. Any copolymerizable unsaturation may be employed, such as acrylate and methacrylate unsaturation. One may also use allylic unsaturation, as provided by allyl alcohol. These, preferably in the form of a hydroxy-functional derivative, as is obtained by reacting a C₂-C₄ monoepoxide, like ethylene oxide, propylene oxide or butylene oxide, with acrylic or methacrylic acid to form an hydroxy ester, are preferably reacted in equimolar proportions with an organic diisocyanate, such as toluene diisocyanate or isophorone diisocyanate. The preferred monoethylenic monoisocyanate is styryl, as in alpha, alpha-dimethyl-m-isopropenyl benzyl isocyanate, and this unsaturated monoisocyanate lacks the ester group so it forms urethanes which lack this group. The amount of the monoethylenically unsaturated isocyanate relative to the monohydric surfactant used in making the macromonomer, (on a mole ratio basis) is typically from about 0.1-2.0 to 1, preferably about 1.0 to 1.0.

Suitable macromonomers useful in this invention can also be represented by the formula:

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wherein:

R^1 is a monovalent residue of a substituted or unsubstituted hydrophobe compound;

each R^2 is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue;

R^3 is a substituted or unsubstituted divalent hydrocarbon residue;

R^4 , R^5 , R^6 are the same or different and are hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue;

and z is a value of 0 to 150.

Illustrative R^1 substituents include, for example, simple or complex hydrophobe containing from 1 to 30 carbon atoms such as alkyl, aryl, aralkyl, alkaryl and cycloalkyl groups.

Illustrative R^3 substituents include, for example, the organic residue of ethers, esters, urethanes, amides, ureas, anhydrides and the like including mixtures thereof. The R^3 substituent can be generally described as a "linkage" between the hydrophobe bearing surfactant or alcohol and the unsaturated portion of the macromonomer compound.

The oxyalkylene moieties included in the macromonomer compounds may be homopolymers or block or random copolymers of straight or branched alkylene oxides. Mixtures of alkylene oxides such as ethylene oxide and propylene oxides may also be employed. Further details concerning the preparation of such macromonomers are known to those skilled in the art and are disclosed, for example, in U.S. Patent

Nos. 4,514,552, 4,801,671, 5,292,828, 5,292,843 and 5,294,693, incorporated herein by reference.

Typically, the amount of the macromonomer is from about 0 to 60 weight percent, preferably from about 0.5 to 50 weight percent and more preferably from about 5 to 40 weight percent based on the total weight of the dispersant polymer. Typically, the molecular weight of the macromonomer ranges from about 400 to 8000 grams per gram mole.

Typically the viscosity of the dispersants of the present invention is from about 5 to 1500 cP in the un-neutralized form measured at 20°C with a 20 to 50 weight percent solids composition using a Brookfield Viscometer with a number 2 spindle at 60 revolutions per minute. The molecular weight of the dispersants of the present invention is typically from about 10^3 to 10^6 , preferably from about 5,000 to 20,000 grams per gram mole. Typically, the particle size of the dispersant is from about 0.05 to 1.0 microns, preferably from about 0.1 to 0.4 microns and more preferably from about 0.1 to 0.3 microns. The Tg of the dispersants of the present invention is typically from about 0 to 90°C preferably from about 5 to 60°C and more preferably from about 15 to 35°C.

When crosslinking functionality is desired, the dispersants useful in the latex compositions of the present invention typically should contain 0.5 to 50% by weight, preferably 20 to 35% by weight, based on the total weight of the dispersant polymer, of at least one monomer having crosslinking functionality.

Any suitable alkali soluble thickeners may be utilized in accordance with the present invention. Suitable alkali soluble thickeners are disclosed, for example, in U.S. Patent Nos. 4,514,552, 4,722,962, 5,292,828 and 5,292,843, which are incorporated herein by reference. Preferred alkali soluble thickeners comprise the aqueous emulsion reaction product of an unsaturated carboxylic acid monomer,

e.g., methacrylic acid; a monoethylenically unsaturated monomer different from the carboxylic acid monomer, e.g. ethyl acrylate; a macromonomer comprising a hydrophobic portion and an alkoxyated portion which is polymerizable with the other monomers. Optionally, the thickener may or may not contain a macromonomer. In the case where no macromonomer is employed, it may be replaced on a equal weight basis with ethyl acrylate, for example. When crosslinking functionality is desired, a monomer having crosslinking functionality such as described above is also introduced to the reaction. The unsaturated carboxylic acid monomer, monoethylenically unsaturated monomer different from the carboxylic acid monomer, macromonomer and crosslinking monomer used to polymerize the thickener can include those such as described above with reference to the binder polymer and dispersant. Often, the macromonomer is a urethane monomer which is the urethane reaction product of a monohydric surfactant and a monoethylenically unsaturated monoisocyanate. Typically, the monohydric surfactant comprises an ethyloxated or propoxylated aliphatic alcohol or alkyl phenol.

In a preferred aspect of the present invention, the thickeners are prepared in accordance using monomers such as those described above with respect to the preferred dispersants. Typically, the amount of the macromonomer is from about 1 to 20 weight percent, preferably from about 5 to 15 weight percent based on the total weight of the polymer.

Typically, the viscosity of the thickeners of the present invention is from about 5 to 1500 cP in the un-neutralized form measured at 20°C with a 20 to 50 weight percent solids composition using a Brookfield Viscometer with a number 2 spindle at 60 revolutions per minute. The molecular weight of the thickeners of the present invention is typically from about 10^4 to 10^7 , preferably from about 20,000 to 200,000 grams

per gram mole. Typically, the particle size of the thickeners is from about 0.05 to 1.0 microns, preferably from about 0.1 to 0.4 microns and more preferably from about 0.1 to 0.3 microns. The Tg of the thickeners of the present invention is typically from about 0 to 90°C, preferably from about 5 to 60°C, and more preferably from about 15 to 55°C.

When crosslinking functionality is desired, the thickeners useful in the latex compositions of the present invention typically contain from about 0.5 to 35% by weight, preferably 1 to 5% by weight, based on the total weight of the thickener polymer, of at least one monomer having crosslinking functionality.

In another aspect of the invention, at least one of the dispersant or the thickener does not have crosslinking functionality. Instead, the level of macromonomer is preferably within the above-stated preferred ranges. Further details concerning suitable dispersants and thickeners are known to those skilled in the art.

The binders, dispersants and thickeners of the present invention are typically in colloidal form, i.e., aqueous dispersions, or in solution and can be prepared by emulsion polymerization in the presence of a chain transfer agent and an initiator. Preparation of latex compositions is well known in the art. Any of the well known free-radical polymerization techniques, e.g., emulsion, solution, suspension or bulk polymerization, used to formulate polymers can be used in the present invention. Such procedures include, for example, single feed, core-shell, and inverted core-shell procedures which produce homogeneous or structures particles. Further details concerning procedures and conditions for emulsion polymerization are known to those skilled in the art. Typically, however, the polymerization is carried out in an aqueous medium at a temperature of from about 35 to 90°C. The pressure is not

critical and is dependent upon the nature of the monomers employed as can be determined by one skilled in the art.

A chain transfer agent is preferably present during the polymerization reaction at a concentration of from about 0.01 to 5 weight percent, preferably from about 0.1 to 2 weight percent based on the total monomer content. Both water-insoluble and water-soluble chain transfer agents can be employed. Illustrative of substantially water-soluble chain transfer agents are alkyl and aryl mercaptans such as butyl mercaptan, mercaptoacetic acid, mercaptoethanol, 3-mercaptopol-1,2-propanediol and 2-methyl-2-propanethiol. Illustrative of the substantially water-insoluble chain transfer agents include, for example, t-dodecyl mercaptan, phenyl mercaptan, pentaerythritol tetramercaptopropionate, octyldecyl mercaptan, tetradecyl mercaptan and 2-ethylhexyl-3-mercaptopropionate.

In carrying out the emulsion polymerization, an initiator (also referred to in the art as a catalyst) is preferably used at a concentration sufficient to catalyze the polymerization reaction. This will typically vary from about 0.01 to 3 weight percent based on the weight of monomers charged. However, the concentration of initiator is preferably from about 0.05 to 2 weight percent and, most preferably, from about 0.1 to 1 weight percent of the monomers charged. The particular concentration used in any instance will depend upon the specific monomer mixture undergoing reaction and the specific initiator employed, which details are known to those skilled in the art. Illustrative of suitable initiators include hydrogen peroxide, peracetic acid, t-butyl hydroperoxide, di-t-butyl hydroperoxide, dibenzoyl peroxide, benzoyl hydroperoxide, 2,4-dichlorobenzoyl peroxide, 2,5-dimethyl-2,5-bis(hydroperoxy) hexane, perbenzoic acid, t-butyl peroxyphthalate, t-butyl peracetate, dilauroyl peroxide, dicapryloyl

peroxide, distearoyl peroxide, dibenzoyl peroxide, diisopropyl peroxydicarbonate, didecyl peroxydicarbonate, dicicosyl peroxydicarbonate, di-t-butyl perbenzoate, 2,2'-azobis-2,4-dimethylvaleronitrile, ammonium persulfate, potassium persulfate, sodium persulfate, sodium perphosphate, azobisisobutyronitrile, as well as any of the other known initiators. Also useful are the redox catalyst systems such as sodium persulfate-sodium formaldehyde sulfoxylate, cumene hydroperoxide-sodium metabisulfite, hydrogen peroxide-ascorbic acid, and other known redox systems. Moreover, as known by those skilled in the art, traces of metal ions can be added as activators to improve the rate of polymerization, if desired.

The particular surfactant useful for conducting the polymerization reaction is not critical to the present invention. Typical surfactants include anionic surfactants such as sodium lauryl sulfate, sodium tridecylether sulfate, diester sulfosuccinates and sodium salts of alkyl aryl polyether sulfonates; and nonionic surfactants such as alkyl aryl polyether alcohols and ethylene oxide condensates of propylene oxide, propylene glycol adducts. Reactive surfactants, i.e., those that can be polymerized with the other monomers used to make the polymer, may be used.

In the preparation of the two-stage latex polymer, the following is a general description of an emulsion polymerization process for preparing alkali-insoluble polymers dispersed in substantially dissolved alkali-soluble polymer. In a typical reaction, the mixture of acrylic or methacrylic acids, acrylate or methacrylate esters, and/or styrenic monomers, the monomer having crosslinking functionality, and other optional ingredients are fed to a reactor where they are emulsion polymerized in the presence of a chain transfer agent and initiator. Typically the polymerization is carried out using a

surfactant or emulsifying agent and in aqueous medium. The temperature can vary from about 35°C to about 90°C or higher; the preferred temperature is from about 70°C to about 85°C. The pressure is not critical and is dependent on the nature of monomers being employed, normally gaseous monomers requiring superatmospheric pressures. At the conclusion of the first stage monomer feed, the reaction is held at reaction temperature until the residual monomer level is less than about 5000 ppmw, followed by addition of the desired neutralizing agent until the first-stage polymer is swollen, partially dissolved, or substantially dissolved. The second-stage monomers, including optional ingredients such as monomers having crosslinking functionality, are then fed into the first-stage polymer medium at the temperatures described above. At the end of the second-stage monomer feed, the reactor is held at temperature for about one (1) hour, cooled and the latex product collected. Optionally the latex may be further neutralized at this time.

Other known additives conventionally used in emulsion polymerization processes may be employed, such as crosslinkers, rheology modifiers, dispersion aids, emulsifiers, photosensitizers, colorants, bactericides, fungicides, etc. Also, other functional monomers, such as those containing wet adhesion functionality may be added. Further details concerning such additives and functional monomers are known to those skilled in the art.

The reaction products of the polymerizations comprising the binders, dispersants or thickeners of the present invention typically have a solids, i.e., polymer, content of from about 15 to 65 weight percent, preferably from about 20 to 65 weight percent and more preferably from about 25 to 60 weight percent based on the weight of the binders, dispersants and thickeners and water.

EXAMPLES

The following examples are provided for illustrative purposes and are not intended to limit the scope of the claims which follow. In addition to the specific examples set forth herein, the examples disclosed in patent application Serial No. 60/138,086 filed June 8, 1999 are incorporated by reference.

Example M1

Preparation of Macromonomer with Small Hydrophobe

To a one-liter glass reactor fitted with a thermometer, heating mantle, thermoregulator, stirrer, nitrogen sparge, and condenser including a Dean-Stark trap was charged 930 grams ("g") of a 40 mole ethoxylate of nonyl phenol, i.e., a small hydrophobe. The reactor contents were heated, with nitrogen sparging, to 110°C and held for two hours while trace moisture was removed and collected in the Dean-Stark Trap (typically less than 1g). The reactor contents were then cooled to 80°C, the Dean Stark trap was replaced with a condenser, and the nitrogen sparge was switched to an air sparge for 15 minutes. With continued air sparging, 0.02 g methoxy-hydroquinone inhibitor, 0.50 g dibutyl tin dilaurate catalyst, and 99.7 g of alpha, alpha-dimethyl-m-isopropenyl benzyl isocyanate (m-TMI, a product of CYTEC, Stamford, CT) were charged in order to the reactor. After a rapid initial exotherm which increased the reaction temperature about 8°C, the contents were maintained at 80°C for an additional two hours. The product was then cooled to room temperature. The final product was a white wax in appearance with residual isocyanate content of 0.5% and with 98% of the original ethylenic unsaturation retained (referred to hereinafter as "macromonomer M1").

Example M2

Preparation of Macromonomer with Large Hydrophobe

A macromonomer was prepared substantially in accordance with Example M1, except that a 40 mole ethoxylate of di-nonylphenol (large hydrophobe) was used in place of the nonylphenol (small hydrophobe) and the amounts of the reactants used were adjusted to maintain a molar ration of 1:1 (referred to hereinafter as "macromonomer M2").

Example A

Synthesis Of Styrene Acrylic Polymer

A monomer mixture was prepared by charging 245g of water, 4.0 g of TRITON™ GR-9M surfactant (Union Carbide Corporation, Danbury, CT), 120 g of styrene, 17 g of methyl methacrylate (Aldrich), 48 g of methacrylic acid (Aldrich), and 30 g of 2 - ethylhexyl acrylate and 25 g of diacetone acrylamide ("DAAM") to a one 2-liter monomer feed cylinder. A second monomer mixture was prepared by charging 250 g of water, 6.0 g of TRITON™ GR-9M, 100 g of diacetone acrylamide, 543 g of methyl methacrylate (Aldrich), and 365 g of 2 - ethylhexyl acrylate into a second 2-liter monomer feed cylinder. A three liter jacketed resin flask equipped with a four - bladed stainless steel mechanical stirrer, Claisen connecting tube, Friedrichs water condenser, nitrogen sparge and bubble trap, thermometer, and monomer addition inlets was used to charge 609 g of water, 8 g of GR-9M (Union Carbide).

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An initial oxidizer solution, prepared by dissolving 3 g of ammonium persulfate in 24 g of water, was prepared in a separate container. A delayed oxidizer solution, prepared by dissolving 6 g of ammonium persulfate in 140 g of water, was also prepared in a separate container. Under nitrogen purge, the reactor was heated to 80°C by circulating temperature controlled water through the reactor jacket. After the temperature of the reactor charge had reached 80°C, the initial oxidizer solution was added to the reactor. Two minutes later, the monomer feed was conveyed to the reaction vessel over a 40 minute period by FMI pumps using 1/8" Teflon tubing with continuous stirring while the reaction temperature was held between 79 - 81°C. The reaction was allowed to proceed at 80°C for an additional fifteen minutes after completion of the monomer feed. To the product was added 20 g of a 30 weight percent ammonium hydroxide solution. After a further 15 minutes the second monomer mix was fed to the reactor concurrently with the delayed oxidizer solution over 2 hours. The product is held at 80 for 1 hour. To the resulting product was added a further 20 g of 15 weight percent ammonium hydroxide solution. The product was then cooled to room temperature. The resulting 48% solids content latex has a pH of 8, and a volume average particle diameter of 93 nanometers("nm") as measured with an Microtrac particle size analyzer (Leeds-Northrop). To the cooled product was added 0.75 molar amounts of adipic dihydrazide based on moles diacetone acrylamide.

Example B

Preparation of Crosslinkable Thickener

A monomer mixture (300 g) was prepared by charging ethyl acrylate ("EA"), methacrylic acid ("MAA"), DAAM macromonomer M2, 13 grams of a 75% solution of TRITON™ GR-9M surfactant and 3 g of

distilled deionized water to a bottle, and dispersing the contents with vigorous shaking. The EA, MAA, DAAM and macromonomer M1 were added in amounts identified in Table 1 below.

A catalyst feed mixture comprised of 0.53 g of sodium persulfate and 52.47 g of water was prepared in another container. To a 2 liter resin flask that had been immersed in a thermostated water bath and equipped with a 4-bladed stainless steel mechanical stirrer, Claisen connecting tube, water condenser, nitrogen sparge and bubble trap, thermometer and monomer and catalyst addition inlets, 1.20 g of the sodium salt of vinyl sulfonic acid and 658.5 g of water were charged. The monomer mixture was charged to a 1-liter graduated monomer feed cylinder, and the catalyst solution was charged to a 125 milliliter graduated catalyst feed cylinder. Under nitrogen purge, the reactor was heated to 70°C, whereupon 33 milliliters of the monomer mixture and 3 milliliters of the catalyst feed mixture were charged to the reaction vessel. The reaction vessel was subsequently heated to 80°C. After allowing the monomers to react for 20 minutes to form a seed product, the monomer and catalyst feed mixtures were conveyed to the reaction vessel by FMI pumps via 1/8 inch teflon tubing at a rate of 1.94 and 0.27 milliliters/minute, respectively, under continuous stirring at a reaction temperature held between 76° and 82°C. The reaction was allowed to proceed for another hour, after which the product was cooled and filtered with a 200 mesh nylon cloth. The coagulum was collected from the reaction vessel and filter cloth. The product is a low viscosity latex of solids content of about 40% and pH of about 2.5.

Table 1 sets forth a variety of thickeners made with the monomers as listed, in accordance with the procedure of Example B. Ingredients are listed in percentages by weight based on the total weight of the polymer.

TABLE 1

<u>Example</u>	<u>M2</u>	<u>MAA</u>	<u>EA</u>	<u>DAAM</u>	<u>Surfactant</u>
B1	15	40	35	10	Rhodafac RE-610
B2	5	40	45	10	Rhodafac RE-610
B3	15	40	40	5	Rhodafac RE-610
B4	5	40	50	5	Rhodafac RE-610
B5	5	40	50	5	Triton GR-9M
B6	5	40	45	10	Triton GR-9M
B7	15	40	35	10	Triton GR-9M
B8	15	40	40	5	Triton GR-9M

Example CPreparation of Non-Crosslinkable Thickener

A monomer mixture (300 g) was prepared by charging ethyl acrylate ("EA"), methacrylic acid ("MAA"), macromonomer M2, 13 grams of a 75% solution of TRITON™ GR-9M surfactant and 3 g of distilled deionized water to a bottle, and dispersing the contents with vigorous shaking. The EA, MAA and macromonomer M1 were added in amounts similar to those identified in Table 1 above.

A catalyst feed mixture comprised of 0.53 g of sodium persulfate and 52.47 g of water was prepared in another container. To a 2 liter resin flask that had been immersed in a thermostated water bath and equipped with a 4-bladed stainless steel mechanical stirrer, Claisen connecting tube, water condenser, nitrogen sparge and bubble trap, thermometer and monomer and catalyst addition inlets, 1.20 g of the sodium salt of vinyl sulfonic acid and 658.5 g of water were charged. The monomer mixture was charged to a 1-liter graduated monomer feed cylinder, and the catalyst solution was charged to a 125 milliliter

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graduated catalyst feed cylinder. Under nitrogen purge, the reactor was heated to 70°C, whereupon 33 milliliters of the monomer mixture and 3 milliliters of the catalyst feed mixture were charged to the reaction vessel. The reaction vessel was subsequently heated to 80°C. After allowing the monomers to react for 20 minutes to form a seed product, the monomer and catalyst feed mixtures were conveyed to the reaction vessel by FMI pumps via 1/8 inch teflon tubing at a rate of 1.94 and 0.27 milliliters/minute, respectively, under continuous stirring at a reaction temperature held between 76° and 82°C. The reaction was allowed to proceed for another hour, after which the product was cooled and filtered with a 200 mesh nylon cloth. The coagulum was collected from the reaction vessel and filter cloth. The product is a low viscosity latex of solids content of about 40% and pH of about 2.5.

Example D

Preparation of Crosslinkable Dispersant

A monomer mixture (300 g) was prepared by charging EA, MAA, DAAM, macromonomer M1, 13 g of a 75% solution of TRITON™ GR-9M surfactant and 3 g of distilled deionized water to a bottle, and dispersing the contents with vigorous shaking. The EA, MAA, DAAM and macromonomer M1 were added in amounts identified in Table 2 below.

A catalyst feed mixture comprised of 0.53 g of sodium persulfate and 52.47 g of water was prepared in another container. To a 2 liter resin flask that had been immersed in a thermostated water bath and equipped with a 4-bladed stainless steel mechanical stirrer, Claisen connecting tube, water condenser, nitrogen sparge and bubble trap, thermometer and monomer and catalyst addition inlets, 1.20 g of the sodium salt of vinyl sulfonic acid and 658.5 g of water were charged. The monomer mixture was charged to a 1-liter graduated monomer feed

cylinder, and the catalyst solution was charged to a 125 milliliter graduated catalyst feed cylinder. Under nitrogen purge, the reactor was heated to 70°C, whereupon 33 milliliters of the monomer mixture and 3 milliliters of the catalyst feed mixture were charged to the reaction vessel. The reaction vessel was subsequently heated to 80°C. After allowing the monomers to react for 20 minutes to form a seed product, the monomer and catalyst feed mixtures were conveyed to the reaction vessel by FMI pumps via 1/8 inch teflon tubing at a rate of 1.94 and 0.27 milliliters/minute, respectively, under continuous stirring at a reaction temperature held between 76° and 82°C. The reaction was allowed to proceed for another hour, after which the product was cooled and filtered with a 200 mesh nylon cloth. The coagulum was collected from the reaction vessel and filter cloth. The product is a low viscosity latex of solids content of about 25%. The product was subsequently neutralized to a pH of about 9.0.

Table 2 sets forth a variety of dispersants made with the monomers as listed, in accordance with the procedure of Example D. Ingredients are listed in percentages by weight based on the total weight of the polymer.

TABLE 2

<u>Example</u>	<u>M1</u>	<u>MAA</u>	<u>EA</u>	<u>DAAM</u>	<u>Surfactant</u>
D1	0	17.5	82.5	0	Triton GR-9M
D2	0	17.5	62.5	20	Triton GR-9M
D3	0	17.5	47.5	35	Triton GR-9M
D4	20	17.5	62.5	0	Triton GR-9M
D5	20	17.5	42.5	20	Triton GR-9M
D6	20	17.5	27.5	35	Triton GR-9M
D7	40	17.5	42.5	0	Triton GR-9M
D8	40	17.5	22.5	20	Triton GR-9M
D9	40	17.5	7.5	35	Triton GR-9M

Example E

Preparation of Non-Crosslinkable Dispersant

A monomer mixture (300 g) was prepared by charging EA, MAA, macromonomer M1, 13 g of a 75% solution of TRITON™ GR-9M surfactant and 3 g of distilled deionized water to a bottle, and dispersing the contents with vigorous shaking. The EA, MAA and macromonomer M1 were added in amounts similar to those identified in Table 2 above.

A catalyst feed mixture comprised of 0.53 g of sodium persulfate and 52.47 g of water was prepared in another container. To a 2 liter resin flask that had been immersed in a thermostated water bath and equipped with a 4-bladed stainless steel mechanical stirrer, Claisen connecting tube, water condenser, nitrogen sparge and bubble trap, thermometer and monomer and catalyst addition inlets, 1.20 g of the sodium salt of vinyl sulfonic acid and 658.5 g of water were charged. The monomer mixture was charged to a 1-liter graduated monomer feed cylinder, and the catalyst solution was charged to a 125 milliliter graduated catalyst feed cylinder. Under nitrogen purge, the reactor was heated to 70°C, whereupon 33 milliliters of the monomer mixture and 3 milliliters of the catalyst feed mixture were charged to the reaction vessel. The reaction vessel was subsequently heated to 80°C. After allowing the monomers to react for 20 minutes to form a seed product, the monomer and catalyst feed mixtures were conveyed to the reaction vessel by FMI pumps via 1/8 inch teflon tubing at a rate of 1.94 and 0.27 milliliters/minute, respectively, under continuous stirring at a reaction temperature held between 76° and 82°C. The reaction was allowed to proceed for another hour, after which the product was cooled and filtered with a 200 mesh nylon cloth. The coagulum was collected from the reaction vessel and filter cloth. The product is a low viscosity latex of

solids content of about 25%. The product was subsequently neutralized to a pH of about 9.0.

The binders, thickeners and dispersants described above were used in the formulation of paints as described below. The paint formulations may, in addition to the polymers described herein, contain conventional additives, such as pigments, fillers, wetting agents, coalescants, biocides and anti-foaming agents and the like.

Example F

Preparation of Latex Paint

A pigment grind is prepared by adding the following ingredients in sequence: 54.96 g of water, 5.92 g of a 28% aqueous ammonia solution and 2.76 g of the Dispersant from Example D9 to a HSD-type grinding apparatus with low agitation. Slowly added are 200.8 g of TiPure R-706 titanium dioxide pigment (DuPont) while the agitation is increased. The mixture is ground for approximately 1 hour, or until a fineness of grind of 8 Hegman is obtained. The agitation is reduced and 25.6 g of ethylene glycol and 1.8 g of BYK 035 defoamer is added.

A thickener premix is prepared by adding 10.32 grams of water to a mix tank and under agitation, adding 0.25 grams of the Thickener from Example B5 and 0.05 grams of 28% aqueous ammonia solution to the tank.

The paint is prepared by adding 568.72 grams of the Binder resin from Example A to the grind mixture under agitation. After this mixture is agitated for about 30 minutes, the following ingredients are added in order: 21.64 g of Exxate 1000 (a coalescing solvent from Exxon), 5.44 g of Arcosolve DPNB (dipropylene glycol n-butyl ether from Arco Chemicals) and 11.64 g of Exxate 900 (oxononyl acetate from Exxon). The thickener premix is then added under agitation. Flash X-150 flash rust inhibitor

(Halox) in an amount of 2.6 g is then added, followed by 1.48 grams of Surfynol 104BC defoamer (Air Products) and 1.48 g of Byk 307 (wetting agent from BYK-Chemie). Dispersant D9 is then added in an amount of 2.76 g. The paint is mixed until it is homogeneous and then reduced with 54.57 g of water to the desired application viscosity.

Example G

Preparation of Paint

A pigment grind is prepared by adding the following ingredients in sequence: 54.96 g of water, 5.92 g of a 28% aqueous ammonia solution and 2.55 g of Dispersant from Example D5 to a HSD-type grinding apparatus with low agitation. Slowly added are 200.8 g of TiPure R-706 titanium dioxide pigment (DuPont) while the agitation is increased. The mixture is ground for approximately 1 hour, or until a fineness of grind of 8 Hegman is obtained. The agitation is reduced and 25.6 g of ethylene glycol and 1.8 g of BYK 035 defoamer is added.

A thickener premix is prepared by adding 10.32 g of water to a mix tank and under agitation, adding 0.25 g of the Thickener from Example B5 and 0.05 g of 28% aqueous ammonia solution to the tank.

The paint is prepared by adding 581.48 grams of the Binder resin from Example A to the grind mixture under agitation. After this mixture is agitated for about 30 minutes, the following ingredients are added in order: 21.64 g of Texanol (Eastman Chemicals), 5.44 g of Arcosolve DPNB (dipropylene glycol n-butyl ether from Arco Chemicals) and 12.73 g of Exxate 900 (oxononyl acetate from Exxon). The thickener premix is then added under agitation. Flash X-150 flash rust inhibitor in an amount of 2.6 g is then added, followed by 1.48 g of Surfynol 104BC defoamer (Air Products) and 1.48 g of Byk 307 (wetting agent from BYK-Chemie). Dispersant D9 is then added in an amount of 2.76 grams.

The paint is mixed until it is homogeneous and then reduced with 45.5 g of water to the desired application viscosity.

Paints were prepared substantially in accordance with the procedure of Examples F and G. The following criteria were used to evaluate the quality of the coatings was made from the paint.

OVEN BAKE

Property	Test Method	Measurement
Gloss		20o
MEK Rubs		Until substrate shows
Salt Spray	ASTM B117	100hrs

The paint was tested according to the above-identified procedures and provided the results shown in Table 3 below.

TABLE 3
PAINT TEST RESULTS

Dispersant	Gloss, 20o	MEK Rubs	Salt Spray, 100hrs
D1	26	95	10.5
D2	29	103	14.25
D3	33	110	18
D4	36	164	17
D5	39	170	20.75
D6	43	177	21
D7	40	230	15
D8	49	238	22
D9	53	246	21.75

While this invention has been described by a specific number of aspects, other variations and modifications may be made without departing from the spirit and scope of the invention as set forth in the appended claims.

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Claims:

1. A polymer polymerized from monomers including:
 - (i) an unsaturated carboxylic acid monomer;
 - (ii) a monoethylenically unsaturated monomer different from the carboxylic acid monomer; and
 - (iii) a macromonomer comprising a hydrophobic portion and an alkoxyated portion which is polymerizable with the carboxylic acid monomer and the monoethylenically unsaturated monomer;characterized in that the monomers further comprise from about 0.5 to 50 wt. %, based on the total weight of the polymer, of at least one monomer having latent crosslinking functionality.
2. The polymer of claim 1 wherein said monomer having crosslinking functionality comprises a carbonyl-containing monomer.
3. The polymer of claim 2 wherein said monomer is selected from the group consisting of acrolein, methacrolein, diacetone acrylamide, diacetone methacrylamide and vinylaceto acetate.
4. The polymer of claim 1 wherein the amount of the monomer having crosslinking functionality is from about 5 to 50 wt. %, based on the total weight of the polymer.
5. The polymer of claim 1 having a number average molecular weight of from about 5,000 to 20,000 g/gmol.
6. The polymer of claim 1 having a number average molecular weight of from about 20,000 to 200,000 g/gmol.

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7. The polymer of claim 1 wherein the amount of the macromonomer is from about 5 to 50 wt. % based on the total weight of the polymer.

8. The polymer of claim 1 wherein the amount of the macromonomer is from about 1 to 20 wt. % based on the total weight of the polymer.

9. A two stage latex binder polymer comprising:

(i) a first stage polymer polymerized from at least one acid or anhydride functional monomer; and

(ii) a second stage polymer polymerized from monomers which are substantially free of acid or anhydride functionality:

characterized in that: (a) the number average molecular weight of the first stage polymer is at least 50,000 g/gmol; and (b) at least one of said first polymer or said second is polymerized from a monomer having latent crosslinking functionality effective to enhance the chemical resistance properties of films formed from the latex polymer.

10. The latex binder polymer of claim 9 wherein said first polymer comprises at least 2 weight percent of the acid or anhydride functional monomer based on the total weight of said first polymer.

11. The latex binder polymer of claim 9 wherein said first polymer comprises at about 5 to 50 weight percent of the acid or anhydride functional monomer based on the total weight of said first polymer.

12. The latex binder polymer of claim 9 wherein said first polymer comprises at about 10 to 20 weight percent of the acid or anhydride functional monomer based on the total weight of said first polymer.

13. The latex binder polymer of claim 9 wherein said first polymer is in a dissolved form.

14. The latex binder polymer of claim 9 wherein said first polymer is in a swollen or partially dissolved form.

15. The latex binder polymer of claim 9 wherein said monomer having crosslinking functionality comprises a carbonyl-containing monomer.

16. The latex binder polymer of claim 15 wherein said monomer is selected from the group consisting of acrolein, methacrolein, diacetone acrylamide, diacetone methacrylamide and vinylaceto acetate.

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(54) Title: WATERBORNE THICKENERS AND DISPERSANTS HAVING IMPROVED CHEMICAL RESISTANCE

(57) Abstract: Improved dispersants and thickeners for use with latex polymers are disclosed which are polymerized from monomers having crosslinking functionality or elevated levels of macromonomers, or both. Latex polymers suitable for use with the thickeners and dispersants of the present invention can be prepared by a two stage polymerization of a first stage polymer and a second stage polymer wherein a monomer having crosslinking functionality is included in either the first stage polymer, the second stage polymer, or both.

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DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that

- (a) My residence and Citizenship are as stated below my name My P O (mailing) address is the same as my residence unless otherwise stated.
 (b) I verily believe I am/we are the original, first and sole/joint inventor(s) of the subject matter that is embraced by and for which a patent is sought on the invention entitled: **WATERBORNE THICKENERS AND DISPERSANTS HAVING IMPROVED CHEMICAL RESISTANCE**

and the specification of which. ☐ is attached hereto (____).
☒ was filed on November 6, 2001 as (UC18024)
 Application No. 10/031803
 and was amended on _____

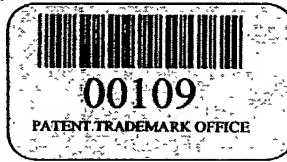
- (c) I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.
 (d) I acknowledge my duty under 37 CFR 1.56 to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in 37 CFR 1.56(b). If this application is a continuation-in-part application, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 CFR 1.56(b) that became available between the filing date of the prior application from which priority is claimed in part (f) below, and the national or PCT international filing date of this application.
 (e) I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate listed below or § 365(a) of any PCT international application that designated at least one country other than the United States of America listed below, and also identify below any other foreign equivalent application for patent or inventor's certificate or any other equivalent PCT international application having a filing date before that of the application on which priority is claimed

Number	PRIOR FOREIGN APPLICATION(S) Country or PCT	Day/Month/Year Filed	PRIORITY CLAIMED	CERTIFIED COPIES INCL.
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- (f) I hereby Claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below, or under 35 U.S.C. § 120 of any United States application(s), or under § 365(c) of any PCT international application designating the United States of America listed below.

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